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Reply: “Liquid-Liquid Phase Transition in Supercooled Yttria-Alumina”

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Greaves *et al.* [1] raise issues regarding our Letter [2] which contested the validity of a reported [3] first-order liquid-liquid transition (LLT) in supercooled $(Y_2O_3)_x(Al_2O_3)_{100-x}$ (or AY x) with $x = 20$. The principal concerns are (1) our use of uncorrected pyrometric temperature data, (2) the accuracy of the composition of our samples, and (3) surface scattering dominating our SANS signal.

(1) An emissivity correction of $\epsilon = 0.92$ [4] implies an underestimate in temperature of 30 K at 2273 K which is small compared to the temperature gradient across a levitated sample (see the pyrometry traces in Fig. 1 of [1]). An emissivity correction does not materially affect the conclusions presented in [2]. The calculated cooling curves in [2] are correct with respect to the explicitly stated molar normalizations.

(2) Gravimetric and electron probe methods show that our sample compositions are reliably reproduced to $\pm 1\%$ [5], consistent with their visual appearance [5]. Also, our AY20 samples supercooled and crystallized at $\simeq 1500$ K, well below the AY15 crystallization temperature of $\simeq 1925$ K [3]. The assertion in [1] that our AY20 sample corresponds to AY15 is mainly from the peak positions and heights in the measured x-ray structure factor $S(Q)$. Fig. 1 shows these parameters (determined from the numerical data sets of [1, 3, 6] and from additional experiments) and also shows that our measured $S(Q)$ for AY20 compares favorably with the revised APS data [1]. Small differences in peak positions are likely to arise from systematic errors in different diffractometer calibrations.

(3) A component of the SANS signal will come from the surface of our levitated sample and, for a spherical sample, will have a cutoff at $Q = 0.015 \text{ \AA}^{-1}$ followed by a Q^{-4} falloff. In the absence of sample density fluctuations this would constitute the only SANS signal. However, calculations based on simple models show that this would not mask a change taking place in the SANS signal from the reported LLT [3]. In contrast, SAXS experiments of the type used in [3] need to stably maintain the sample and incident beam positions to better than 10 \mu m .

Greaves *et al.* [1] interpret the pyrometry data from our SANS experiment (trace B in their Fig. 1) as arising from a polyamorphic rotor, *without* reference to any other

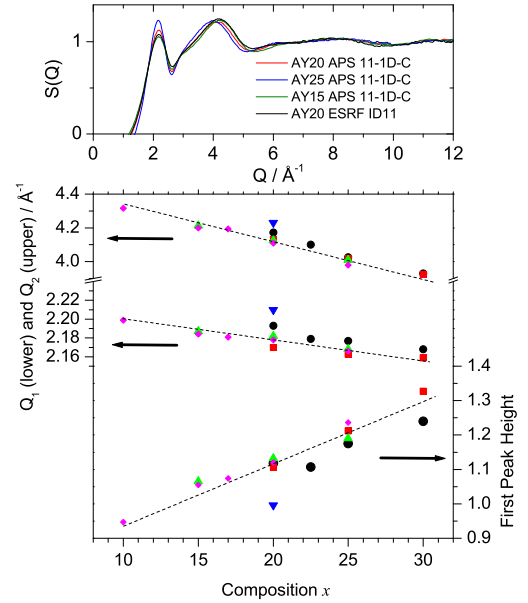


FIG. 1. Upper panel. Comparison of the $S(Q)$ measured for our AY20 sample [2] and for several different compositions at the Advanced Photon Source (APS) [1]. Lower panel. Composition dependence of the first and second peak positions and the first peak height in $S(Q)$. Our ESRF data [6] (\bullet), old APS data [3] (\blacktriangle), Daresbury data [3] (\blacktriangledown), and revised APS data [1] (\blacklozenge). The peak heights from [6] have been shifted by 0.3 to achieve alignment.

experimental observations. The temperature variations were, however, clearly observed to result from a small gas bubble in the sample which led to rotational instability. Given the evidence in (2) that our sample is AY20, the assumption of a polyamorphic rotor would imply a second LLT in AY20 at 1927 K, an unlikely scenario.

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